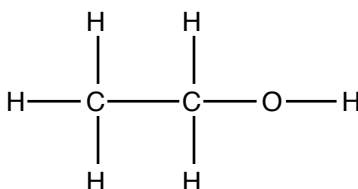


Experiment 14: A Kinetic Study of the "Breathalyzer" Reaction

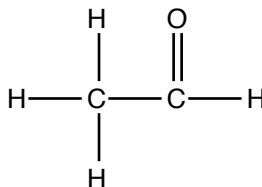
Objective: In this experiment, you will study the kinetics of the reaction of ethanol and acidic potassium dichromate to determine whether the reaction is zero, first or second order with respect to dichromate concentration and to determine the rate constant of the reaction.

Introduction

In the 1960's, as concern over the increasing number of injuries and fatalities caused by drunken drivers began to rise, chemists looked toward the development of simple screening tests that could be used by police officers to determine the level of alcohol in the blood of a car operator. Drinking alcohol, referred to by chemists as **ethanol**, has the following chemical structure:

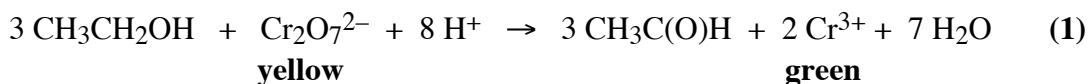


It can react with a variety of oxidizing agents to produce the compound **acetaldehyde**, which has the structure shown:



One oxidizing agent that will accomplish this transformation is potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. (See Tro, pp 928-932, for further discussion regarding alcohols and aldehydes.)

Potassium dichromate produces a yellow solution when dissolved in acid. As an acidic solution of dichromate reacts with ethanol, the Cr(VI) species is reduced to a Cr(III) species, which is green in aqueous solution. The overall reaction is as follows:



Because the reaction is accompanied by this dramatic color change, it is possible to monitor it spectrophotometrically.

In a "Breathalyzer", a portable instrument used by the police to test alcohol levels in the blood, the breath is passed through an ampoule that contains an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and sulfuric acid. Alcohol contained in the breath is then oxidized to acetaldehyde while the chromium in the ampoule is reduced to the Cr(III) species. Light

of the appropriate wavelength (440 nm) is passed through the ampoule and compared to a reference solution that contains only acidic potassium dichromate. The absorbance difference between the two solutions is then interpreted to give the percent of ethanol contained in the blood.

The color change associated with the oxidation of ethanol also provides a convenient means for studying the *kinetics*, or rate, of the reaction (see Tro, Chapter 13, especially pp 564-581). The complete rate equation for reaction (1) has the form:

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k[\text{Cr}_2\text{O}_7^{2-}]^x[\text{CH}_3\text{CH}_2\text{OH}]^y[\text{H}^+]^z \quad \text{Eq. 1}$$

where k is the **rate constant**, t is the time, the quantities in brackets indicate concentration of the reactants, and the values for x , y and z must be determined experimentally. However, under conditions where the concentrations of ethanol and acid are large (and therefore remain approximately constant throughout the reaction), the rate equation reduces to:

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k[\text{Cr}_2\text{O}_7^{2-}]^x \quad \text{Eq. 2}$$

The objective of this experiment is to determine whether $x = 0$, 1 or 2; that is, whether the rate law is zero, first or second order with respect to dichromate.

Let us examine each case individually. If we let the initial concentration of dichromate ion equal a , and the concentration of dichromate which will have reacted at time t equal c , then the concentration of dichromate that remains at t is equal to $(a - c)$. The rate equation becomes:

$$+\frac{dc}{dt} = k(a - c)^x \quad \text{Eq. 3}$$

For a zero order reaction, $x = 0$ and the rate equation reduces to:

$$+\frac{dc}{dt} = k \quad \text{Eq. 4}$$

Integrating, we obtain:

$$c = kt \quad \text{Eq. 5}$$

In this case, a plot of concentration, c , versus time, t , will produce a straight line with the slope equal to the rate constant, k .

For a first order reaction, $x = 1$ and the rate equation is:

$$+\frac{dc}{dt} = k(a - c) \quad \text{Eq. 6}$$

Integrating, we obtain:

$$\ln [a / (a - c)] = kt \quad \text{Eq. 7}$$

Thus, a plot of $\ln [a / (a - c)]$ versus t will produce a straight line with a slope of k .

Finally, for a second order reaction, $x = 2$ and the rate equation is:

$$-\frac{dc}{dt} = k(a - c)^2 \quad \text{Eq. 8}$$

Integrating, we obtain:

$$1/(a - c) = kt + 1/a \quad \text{Eq. 9}$$

In this case, a plot of $1/(a - c)$ versus t will give a straight line with a slope of k and a y-intercept of $1/a$.

In order to determine the quantities a and c , we must convert the absorbance of the solution at a wavelength of 440 nm to the concentration of dichromate ion in solution. Recall Beer's Law (see Experiment 6):

$$A_0 = \epsilon a \ell \quad \text{Eq. 10}$$

where A_0 = initial absorbance of the solution, a = initial concentration of dichromate ion, ℓ = path length of the cell and ϵ = the molar absorptivity constant. Rearranging equation 10:

$$a = A_0/\epsilon \ell \quad \text{Eq. 11}$$

At time t , the equation becomes:

$$a - c = A_t/\epsilon \ell \quad \text{Eq. 12}$$

where A_t is absorbance of the solution at time t . Substituting equation 11 and rearranging:

$$c = (1/\epsilon \ell)(A_0 - A_t) \quad \text{Eq. 13}$$

For the zero order reaction equation, making the appropriate substitution for c into equation 5 results in the following equation:

$$A_t = A_0 - k(\epsilon \ell)t \quad \text{Eq. 14}$$

A plot of A_t versus t will produce a straight line for a zero order reaction with the slope equal to $-k(\epsilon \ell)$ and a y-intercept equal to A_0 .

To obtain the quantity $a / (a - c)$ in terms of absorbance values for a first order reaction (equation 7), we must divide:

$$a / (a - c) = (A_0/\epsilon \ell) / (\epsilon \ell / A_t) = A_0/A_t$$

$$\ln (A_0/A_t) = kt \quad \text{or}$$

$$\ln A_t = \ln A_0 - kt \quad \text{Eq. 15}$$

Thus, a plot of $\ln(A_t)$ versus t will produce a line with a slope equal to $-k$ and a y-intercept equal to $\ln(A_0)$ for a first order reaction.

Lastly, substituting absorbance values into equation 9 gives:

$$1/A_t = (k/\epsilon\ell)t + 1/A_0 \quad \text{Eq. 16}$$

where a plot of $1/A_t$ versus t gives a straight line with a slope equal to $k/\epsilon\ell$ and a y-intercept of $1/A_0$ for a second order reaction.

A correction must be introduced at this point. When the reaction reaches completion, at $t = \infty$, there will remain some absorbance of light at a wavelength of 440 nm. This residual absorbance, A_∞ , must be subtracted from each absorbance term in equations 14, 15 and 16:

$$(A_t - A_\infty) = (A_0 - A_\infty) - k\epsilon\ell t \quad \text{Eq. 17}$$

$$\ln \left[\frac{(A_0 - A_\infty)}{(A_t - A_\infty)} \right] = kt \quad \text{Eq. 18}$$

$$\frac{1}{(A_t - A_\infty)} = \left(\frac{k}{\epsilon\ell} \right) t + \frac{1}{(A_0 - A_\infty)} \quad \text{Eq. 19}$$

Procedure (outline the steps of this section for your pre-lab assignment)

Two students will be assigned to work together to prepare one reaction solution. Each pair will be assigned to a specific spectrophotometer, which they must use to acquire all their measurements throughout the course of the experiment.

Set the wavelength of the Novaspec or Genesys 20 spectrophotometer at 440 nm. Fill a clean, dry cuvet with distilled water, and use this to "zero" the instrument (see TECH V).

CAUTION: Compounds that contain chromium (VI) are toxic and suspected carcinogens. Wear gloves. Wash your hands thoroughly with soap and water after handling solutions that contain Cr(VI). Do not pour any solution containing chromium down the sink!

Using a volumetric pipet, transfer 5 mL of 0.0196 M potassium dichromate, $K_2Cr_2O_7$, solution into a clean, dry 125 mL Erlenmeyer flask. Add 50 mL of 3.9 M sulfuric acid, H_2SO_4 , to the flask using a graduated cylinder, and swirl the flask well to thoroughly mix the solution.

Fill a new clean, dry cuvet with this acidic dichromate solution. Wipe off the outside of the cuvet with a Kimwipe so that is clean and dry, and place it in the spectrophotometer. Record the absorbance of the acidic dichromate solution in your notebook (this is the initial absorbance, at $t = 0$).

Remove the cuvet from the instrument, and pour the contents back into the Erlenmeyer flask. Your instructor will add 0.13 mL of ethanol to the solution via syringe. **Note the time of addition of the ethanol (to the nearest second)**, and record it in your notebook. Quickly and carefully swirl the solution, then rinse and fill the cuvet and return it to the Novaspec or Genesys 20. Close the lid and record the absorbance of the solution along with the time. Try to read the absorbance 60 seconds after the addition of ethanol.

Continue to take readings of the absorbance and the corresponding time at 60 second intervals for 7 minutes total. At the end of this time, remove the cuvet from the spectrophotometer, and allow it to stand undisturbed at room temperature for at least one hour. You may proceed with the set-up of the spreadsheet for your data at this time.

Re-zero the spectrophotometer. Return the cuvet containing the reaction mixture to the instrument and record the final absorbance value (A_{∞}). When you have completed the experiment, pour all solutions into the appropriate **Laboratory Byproducts Jar**.

Data Work-up (you do not need to outline the steps of this section for your pre-lab assignment)

You will use the spreadsheet program Excel to analyze your data (see TECH IV.C). To log onto the computer, click on “Student” and type “chemistry” for the password, then click on **Log In**. Click on the **Applications** folder at the bottom of the screen. In the window that opens, click on the button labeled Excel. Under the **View** menu, make sure that **Formula Builder** has a check mark next to it. You can begin by deciding what data you wish to include in the table. You will need to plot three different graphs (or *charts*) in order to determine whether or not the reaction that you studied is zero, first or second order. Let’s use the zero order case as an example to get you started.

In the case of a zero order reaction, we need to plot $A_t - A_{\infty}$ as a function of time, t , in order to obtain a straight line (see equation 17). You can place your cursor in the first cell (A1) and type the word *time* with the units in parentheses, then press the **return** key. In the cell below this (A2), you can type the first value for time, which is zero. In the next cell down (A3), type the next value for time, which should be approximately 60 seconds (if you did not take your first absorbance reading exactly one minute after the addition of ethanol, write down the exact time value). Continue to enter the time values down column A.

You can label the next column (B) with the heading $A(t)$, and then enter the absorbance values that correspond to the time values in the cells of column B. We need to enter the value for the final absorbance reading, A_{∞} , somewhere in the table. Choose a cell that will not be used for any other data entries, such as A11, and type $A(f)$ (for *final* absorbance reading, since the symbol ∞ is not available) in this cell. In the next cell over (B11), type the value that you obtained for the final absorbance reading. [While you are waiting to obtain this value, type 0.05 as a “dummy” value in this cell for now. You can change it later.] Your table should look similar to the one shown at the top of the next page.

We are now ready to define a column that will contain the values for $A_t - A_f$. First, place a heading at the top of column C for this data, $A(t) - A(f)$. We will now define a function for each cell in column C so that the computer will calculate the value $A_t - A_f$ for us. In cell C2 we would like the computer to subtract A_f (located in cell B11) from the value for A_t , which is located in cell B2. To do this, you could place the cursor

Time (sec.)	A(t)
0	0.602
60	0.505
120	0.403
180	0.301
240	0.251
300	0.202
360	0.154
420	0.111
A(f)	0.055

in cell C2 and type:

$$=B2-B11$$

A number would appear in cell C2 that corresponds to the first value for A_t minus the value for A_f . You could continue to define a similar function in each individual cell of column C (e.g. cell C3 would be: $=B3-B11$).

Instead of typing a similar formula over and over, it is easier to use an **array** to define the whole column at once. To do this, simply highlight all the cells that will be defined with a similar function (cells C2 through C9, in this case). Then type:

$$=B2:B9-\$B\$11$$

Remember the equal sign! The dollar signs that precede the letter and number in the above formula ensure that the address of this cell (B11) remains constant throughout the array. Now *hold down the command key* (⌘), and then press the **return** key, and the appropriate numbers should appear in all the highlighted cells. (Array formulas must be locked in with the command-return keys.) [Note: To delete an array, all of the cells involved in the array must be highlighted, and then the command **Clear** is chosen from the **Edit** menu followed by pressing the command-return keys.]

You can complete the next columns on your own. Decide what you need to plot in the cases of a first order reaction and a second order reaction (see equations 18 and 19), and label the columns appropriately. Then, define the necessary functions for the cells in those columns. Be sure to *save* your data at some point. It is a good idea to save the data periodically as you work on your spreadsheet.

Some hints:

The value for A_0 is contained in one of the cells of the table. Which one?

The command for obtaining the natural log of a value is simply LN followed by the argument in parentheses. For example, if you wanted to take the natural log of a value in cell A1 you would type: =LN(A1)

The square brackets, [], should not be used when typing mathematical formulas in Excel. Use parentheses— these can be nested several times.

Example: =(A1*(B1/(A2+B2)))

Charts

To obtain a graph of your data, you need to highlight the cells in the first column (the time values). Next, *hold down the command key* and highlight the cells in the column corresponding to the values necessary for a zero order plot (C2 to C9). It is important that the column containing the x values (time) is highlighted first. Do *not* highlight the text headings of the columns. Once both columns are properly highlighted, pull down the **Insert** menu and choose **Chart**. Click on the button **XY (Scatter)** from the row of Chart options, then click on the picture of data points without a line drawn through them. A plot should appear on the spreadsheet. Pull down the **Chart** menu and select **Move Chart...**. In the box, that appears, click in the circle next to “New sheet”, then click on **OK**. The chart will now fill the screen as it appears on its own page. Pull down the **View** menu and choose **Formatting Palette**. Use the palette that appears to give your plot a title and to label the axes. Be sure the Chart Options section of the Palette is visible (click on the triangle if it is not). In the pull-down menu at the top of the Chart Options, choose Chart Title. Click in the box underneath this menu and type in a title for your plot. Next, change the Chart Title in the pull-down menu to Horizontal (Category) Axis. Again, click in the box below and type a title for the x -axis. Repeat the procedure for the Vertical (Value) Axis to type a title for the y -axis.

You can add a “best fit” line by placing the cursor on a data point of the graph and clicking once. All of the data points should now be highlighted. Pull down the **Chart** menu and choose **Add Trendline**. In the box that appears, click on **Line** from the list in the left-hand column. Next, click on **Options**. Click to put \checkmark 's in the boxes for “Display equation on chart” and “Display R-squared value on chart”, then click **OK**. Print your graph by choosing **Print** from the **File** menu.

To get back to the worksheet, click on the tab at the bottom of the screen that says **Sheet 1**. Use the same procedure to obtain plots and print-outs for the first and second order data as well. Determine which plot produced the straightest line, and thus, whether the reaction is zero, first or second order.

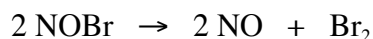
If you have trouble deciding which plot produced the straightest line, you can look at the value for R^2 , which is displayed on the chart. R is called the correlation coefficient and gives an indication of the “goodness” of fit of the data. The closer the R^2 value is to 1.00, the better the data fit, or correlate, to a straight line.

Once you have determined the order of the reaction rate, you can find the slope of this line and thus, the rate constant. The slope of the line is found in the equation that is displayed on the chart. Alternatively, you can use the **LINEST** function to perform a linear regression on the selected data and display the slope and the y -intercept on the worksheet.

When you have completed the worksheet, save it and print it out by choosing **Print** under the **File** menu.

Calculations

1. Hand in the three plots (zero, first and second order) and the Excel worksheet of your data and results.
2. Is the reaction zero, first or second order with respect to dichromate?
3. What is the value of the rate constant? What are the units? Use the value $3.58 \times 10^2 \text{ M}^{-1}$ for $\epsilon\ell$, if necessary.
4. Thermal decomposition of nitrosyl bromide to nitric oxide and bromine occurs according to the following reaction:



The rate law is:

$$\frac{-d[\text{NOBr}]}{dt} = k[\text{NOBr}]^x$$

The equations corresponding to the possible orders of the reaction follow:

$$\begin{aligned} \text{zero order: } [\text{NOBr}] &= [\text{NOBr}]_0 - kt \\ \text{first order: } \ln([\text{NOBr}]_0/[\text{NOBr}]) &= kt \\ \text{second order: } 1/[\text{NOBr}] &= kt + 1/[\text{NOBr}]_0 \end{aligned}$$

Use Excel to determine the order and rate constant of the reaction given the following data:

Time (s)	[NOBr] (M)
0	0.150
20	0.0759
40	0.0494
60	0.0380
80	0.0306
100	0.0244
120	0.0214

Note that in this problem you are given the *concentration* of NOBr (in molarity), **not** the absorbance of a solution of NOBr. You do not need to use the Beer's law relationship between absorbance and concentration to solve this problem. Plot the "best fit" line. Hand in the relevant plots and data tables.

Questions

1. If you wished to alter the rate of the reaction of dichromate with ethanol, what changes could you make in the experimental conditions? Name two.
2. Discuss the sources of error present in this experiment and how they would affect your results.